	extstyle ext	$^{ m Jl}_{ m imes 10^{-5}}$	$^{\eta 1}_{ imes \ 10^7}$	${ au l \over imes 10^2}$	$\overset{J2}{\times 10^{-5}}$	$\eta^2_{10^6}$	$^{ au2}_{ imes10}$	$\overset{J3}{\times 10^{-5}}$	$^{\eta 3}_{ imes \ 10^5}$	$^{ au 3}_{ imes \ 10}$	$rac{\eta \mathrm{o}}{ imes 10^8}$
940 N U	1·4 2·0	1·0 1·3	10 2·8	11 3·6	1·0 1·2	17 1·5	14 1·8	1.5	12	1.8	3·0 3·8
941 N U	10 9·7	41 14	·25 ·40	10 5·4	13 16	1·1 ·22	14 3·6	40	·41 —	1·7 —	·01 ·52

Table 1. Model analysis for 3% w/w Carbopol 940 and 941 Systems.

N = Neutralized, U = Unneutralized, J = Compliance, dyne⁻¹ cm². η = Viscosity poise τ = Retardation time, s.

Unneutralized Carbopol 940 and 941. Flow curves were similar but showed a marked decrease in consistency compared with neutralised systems. Carbopol 941 gels increased in hysteresis with increase in concentration. The creep curves approached Hookean behaviour and calculated parameters were of the same order as those derived from neutralized gels. This indicates that in their rheological ground state the neutralized and unneutralized systems are similar, but when tested at high shear rates differences in structure become apparent (i.e. strong electrostatic repulsion between ionized carboxy groups and weak hydrogen bonding between undissociated carboxy groups).

Subjective differences at tertiary level (Sherman, 1971)–940 gels were creamy and viscous, 941 preparations were sticky and elastic.

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The influence of alcohol chain length on the structure and rheology of emulsions stabilized by ceto-macrogol/long chain alcohols $% \left(\frac{1}{2}\right) =0$

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Previous studies showed that alcohol structure markedly affects the consistencies of o/w emulsions stabilized by ionic surfactant/long chain alcohol mixed emulsifiers (Eccleston & Barry, 1973). This present work investigates the influence of alcohol chain length and homologue composition on the rheological stability of non-ionic cetomacrogol emulsions.

Liquid paraffin emulsions prepared with cetomacrogol and alcohols tetradecanol (A), hexadecanol (B), octadecanol (C) and cetostearyl alcohol (D) were examined by microscopical, particle size analytical and rheological (continuous shear, small strain creep and oscillation) techniques at 25° as they aged over 30 days.

The particle sizes of the emulsions were similar, and did not increase with age. Thus, as in previous work, rheological stabilities were not correlated with particle size distributions, but rather with viscoelastic networks formed in the continuous phases when non-ionic mixed emulsifiers interact with water (Barry & Eccleston, 1973).

The rheological properties of emulsions A and B differed from C. Emulsion D, of mixed homologue composition, showed properties of all three emulsions prepared with the pure alcohols. A and B were semisolid immediately after preparation and of a similar consistency. This was shown in oscillation by the similar values for amplitude ratios and phase lags throughout the frequency range $25 \times 10^{-3} - 25$ Hz and in creep by similar total compliances. Continuous shear data, however, indicated that A was more resistant to breakdown at high shear rates. The apparent viscosities derived for a standardized shearing cycle were considerably greater for A. Emulsion C was so mobile after preparation that initial oscillatory and creep data were not derived. Apparent viscosities were considerably below those of A and B.

On ageing, the consistencies of A and B changed during the first 10 days and then remained essentially constant. The changes were shown in A by maxima in apparent viscosities and amplitude ratios and minima in phase lags and total compliances, and in B by decreasing apparent viscosities and amplitude ratios and increasing creep compliances and phase lags over the first 10 days. Thereafter, these parameters did not change markedly. In contrast, C exhibited considerable consistency increases on ageing, particularly over the first few days, when the emulsion changed from a mobile liquid to a semisolid. Emulsion D was semisolid initially (as A and B) but showed considerable consistency increases during the first 2 days (as C). Thereafter consistency changes were slight. Apparent viscosities indicated that D was more resistant to breakdown than the other emulsions.

Microscopical examinations supported the view that networks formed in C differed from those in A and B, and that those formed in D were the most extensive. Although the ceto-macrogol/pure alcohol networks were diffuse, they did not rapidly disintegrate on storage as did the ionic surfactant/pure alcohol networks examined previously.

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Transit in free films: casting solvent effects

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The permeability of polymer films may be affected by varying the solvent(s) used in casting (Johnston & Sourirajan, 1973). Permeation rate for urea has been shown to be greater when the lower side of acrylic-methacrylic ester copolymer film is exposed to the solute (upper-lower side-difference) (Anderson, Armstrong & Abdel-Aziz, 1973). Casting solvent variation is now shown to determine permeation rate and degree of side-difference in acrylic-methacrylic ester copolymer (Eudragit RL100, Rohm and Haas) film which was cast from acetone and acetone plus variable methanol or ethanol content. Films were mounted in a permeability cell such that one side was exposed to 10% w/v aqueous urea solution and the other to water; the urea appearing in the acceptor compartment being determined (Watt & Chrisp, 1954). Lower and upper surfaces of the film were exposed to solute in the donor compartment, these terms signifying contact with casting substrate or atmosphere respectively during casting.



FIGS. 1 and 2. Effect on permeability of solvent additives in film casting solutions. Fig. 1. 10% w/w methanol or ethanol in acetone in the casting solvent. Fig. 2. 3 h values with variable alcohol levels. w = quantity (g) urea transferred to the acceptor cell. Acetone, \blacklozenge lower surface, \diamondsuit upper surface; ethanol, \blacktriangle lower surface, \bigtriangledown upper surface; methanol, $\textcircled{\bullet}$ lower surface, \bigcirc upper surface.